JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 69A, No. 2, March–April 1965

Relative Enthalpy of Polytetrafluoroethylene From 0 to 440 °C[1]

Thomas B. Douglas and Ann W. Harman

(November 18, 1964)

Using a drop method and an ice calorimeter, precise measurements of enthalpy relative to 0 °C were made on a sample of granular polytetrafluoroethylene which was initially 95 percent crystalline. The measurements were at temperatures every 50 degrees from 50 to 300 °C (both before and after melting and quenching); and also at 340, 400, and 440 °C in the liquid range, where it appeared that structural equilibrium of the polymer was reached only slowly. Marked upturns in the heat capacity-temperature curves of the crystalline and quenched polymer above about 200 °C were treated as corresponding to gradual but reversible fusion of the type commonly caused by impurity components ("premelting"). Consideration was given also to the possibility of melting of thin crystals. The (total) heat of fusion could not be determined calorimetrically by the method used, but the additional assumption of three alternative approximations in all cases led to 327 °C as the crystalline melting point of the polymer, which agrees exactly with the accepted value based on direct observation. The heat capacity and relative enthalpy and entropy of the polymer derived from the data were joined smoothly with precise low-temperature values measured earlier at the Bureau on the same and two other samples of polytetrafluoroethylene, and these properties are represented by equations and tabulated as functions of temperature.

1. Introduction

Polytetrafluorethylene, $(C_2F_4)_n$, which is commercially produced under the trade name "Teflon",[2] has many properties which make it unique among known high polymers. Its crystalline melting point (327 °C), viscosity when melted, and thermal stability are especially high. It is highly resistant to chemical attack, and is insoluble in all common solvents. It has an extremely low dielectric loss and high dielectric strength. Also, it has unique non-adhesion and antifrictional characteristics. These properties suggest some of the more important practical uses of this unusual polymer.

During the past two decades numerous investigations of the properties and molecular-scale structure of polytetrafluoroethylene have been published. A comprehensive review of the subject, with numerous references, was published by Sperati and Starkweather in 1961 [1].[3]

Of the various kinds of polytetrafluoroethylene, one is the so-called "granular" polymer. It consists of spongy white particles whose porosity is confirmed by the fact that the specific surface area as determined by nitrogen adsorption is over 1000 times as great as the outer surface area of the particles observed microscopically.

The covalent chains forming the molecules of polytetrafluoroethylene are believed to be entirely "linear" (i.e., unbranched), a belief which receives support from the fact that the formation of branched chains in the polymerization of C_2F_4 would involve the breaking of C–F bonds, which are relatively strong [1]. The average number of CF_2 groups per chain has been found to vary from 3,000 for specially prepared low-molecular-weight samples to as high as 180,000 for samples similar to those of industrial interest [1], these numbers corresponding to molecular weights 50 times as great. It is considered highly probable that each molecule of the polymer contains a sulfonic or a carboxyl group at each end, depending on the type of initiator used in the polymerization [1]. Samples obtained by direct polymerization are in some cases over 95 percent crystalline, but after having been melted the degree of crystallinity is invariably decreased. Infrared absorption and x-ray diffraction studies by Thomas et al. [2] indicated that after quenched, intermediate, and slow cooling from the melt, the degree of crystallinity was approximately 50, 60, and 70 percent respectively. However, electron-microscope studies led Speerschneider and Li [3] to believe that similar variations of cooling rate led to little difference in the degree of crystallinity; they postulated alternate layers of crystalline and amorphous material in the polymer so treated. The rate of crystallization varies inversely with molecular weight. The density at room temperature varies from 2.3 g cm^{-3} for the crystalline to 2.0 g cm^{-3} for the amorphous polymer [1].

In crystalline polytetrafluoroethylene at temperatures below 19 °C the chains are arranged in helices with a 180° twist every 13 carbon atoms. As the temperature rises, at atmospheric pressure a crystal-disordering transition occurs at approximately 19°, and another much smaller one at 30 °C, with gradual untwisting and disorientation of the chain segments

---

[1] This paper is based on work sponsored by the Ordnance Corps, U.S. Department of the Army.

[2] Registered trademark of E. I. du Pont de Nemours and Company, Wilmington, Delaware.

[3] Figures in brackets indicate the literature references at the end of this paper.

until above 30° the preferred crystallographic direction has been lost and these segments oscillate about their long axes, with some indication of occasional complete rotations. In the amorphous regions of the polymer, glass transitions have been detected at about −97° and 127 °C, where motions of sequences of CF_2 groups are believed to set in. Eby and Sinnott [4] believed that the rise of internal friction above 240 °C in a 95-percent-crystalline sample may be the result of additional but hitherto unresolved crystalline relaxations. The generally accepted melting point of the crystalline polymer is 327 °C, where all opacity was observed to disappear on heating [5]. However, a small crystalline relaxation just below this temperature has been observed, and this is attributed to melting of crystallites. Symons [6] has recently reported that polytetrafluoroethylene, as crystallized from solution in perfluorokerosene, remained unchanged in appearance at temperatures below 327°, but showed a very gradual loss of birefringence and overall form through the range 327–347° on further heating at a rate of 0.5 deg per min. The high melting point of the polymer is attributed to the persistence of direction of the long molecular chains. A considerable amount of molecular-scale structure persists on melting. X-ray diffraction shows that in the liquid the chains are almost straight for several repeat units; Sperati and Starkweather [1] believe that the chains are folded (over long periods), as they are in other polymers. As the temperature of the melted polymer rises, pyrolysis begins to occur (by first-order reaction in the range 360–510 °C), C_2F_4 being the major gaseous decomposition product. During pyrolysis the average molecular weight and viscosity of the liquid decrease.

Most of the fundamental thermodynamic properties of different types of polytetrafluoroethylene have been measured. Data-of-state measurements include the density under various conditions (including thermal expansion to high temperatures and compressibility to high pressures), as well as the change of melting point with pressure. The standard heat of formation has been determined by fluorine-combustion calorimetry. Furukawa, McCoskey, and King [7] measured the relative enthalpy and the heat capacity of four samples (powdered, annealed, quenched, and molded) from 15 to 370 °K (i.e., up to 97 °C), estimating their heat-capacity values for a given sample to be accurate in general to ±0.2 percent. Later, Marx and Dole [8] reported measurements of the heat capacity of two samples (powdered and drawn) from −25° to 120 °C. (For the powdered form, Marx and Dole's heat capacities are, between −23° and 0 °C, about 3.5 percent lower than those of Furukawa et al., but agree much more closely above 40 °C.) These various thermodynamic data have been used by others to calculate other thermodynamic properties and to elucidate further the structure of the polymer. McGeer and Duus [9] and Lupton [10] have calculated the crystalline heat of fusion, and Starkweather and Boyd [11] have decomposed the entropy of fusion into components attributed to specific structural changes. Brandt [12] has developed an intermolecular potential function and estimated the lattice energy and the compressibility at 0 °K. Gotlib and Sochava [13] have used the method of Born and von Karman to calculate from spectroscopic data a frequency spectrum for polytetrafluoroethylene, reporting good agreement with the measured heat capacities of the polymer in the range 50–200 °K.

The present paper reports measurements by drop calorimetry of the enthalpy relative to 0 °C of polytetrafluoroethylene. The sample on which the measurements were made and that measured by Furukawa, McCoskey, and King [7] at lower temperatures and referred to by them as granular powder were actually specimens from the same batch of material. Before the sample had been melted, the heat capacities of the present work agree well with the values of Furukawa et al. on the powder, but after the sample had been melted the heat capacities became considerably higher but agreed approximately with their values on the annealed and molded forms.

2. Sample

Only one sample of polytetrafluoroethylene was used for the present enthalpy measurements. The sample was obtained from E. I. du Pont de Nemours and Company in 1951 as "Teflon TF-1", and is equivalent to their current commercial product designated as "Teflon 1 TFE fluorocarbon resin."

Recently, through the courtesy of C. A. Sperati, several tests were carried out at du Pont on a third sample of the same batch in order to characterize it more definitely in case its properties should bear a significant relation to the precise thermal results reported here. The results of these tests were summarized as indicating that the sample is of commercially available ASTM[4] Type I granular polytetrafluoroethylene (ASTM designation D–1457–62T), the particular sample having a crystalline content of 94.8 percent, a specific surface area of 2.2 $m^2\ g^{-1}$, and a standard specific gravity of 2.166. The average molecular weight, which was not measured directly, was believed to be relatively very high. As discussed in other sections of this paper, the above properties of the sample were drastically changed before the series of thermal measurements was completed, especially at the time when the sample was first heated above its melting point.

Before the thermal measurements, the sample specimen was evacuated to remove traces of moisture, and, though unsealed in its container, showed no detectable loss in mass during the subsequent periods of heating to temperatures as high as 340 °C. In the thermal measurements the sample was in a cylindrical container of pure nickel weighing about 20 g. A screw lid of the same material closed the container, but not gas-tight. Before each in-

---

[4] American Society for Testing Materials.

sertion into the apparatus, filled with helium at atmospheric pressure, the container with sample was evacuated and filled with the same gas.

3. Calorimetric Procedure

The apparatus and method used in measuring the enthalpy have been described in detail in a previous publication [14]. In brief, the method was as follows. The sample container was suspended in the center of a silver-core furnace until, as determined by preliminary "relaxation-time" tests [15], the sample had time to reach the constant furnace temperature within 0.01 deg C or less. The sample and container were then dropped (with almost free fall) into a precision Bunsen ice calorimeter, and the heat they delivered in cooling to 0 °C was determined by the mass of mercury entering the calorimeter because of the reduction in volume caused by the melting of ice. Similar measurements had been made on the empty container to account accurately for (a) the part of the heat which was due to the container when the sample was present, and (b) the small amount of heat lost elsewhere than to the calorimeter during the drop. The net heat contributed by the sample itself is taken as its change in enthalpy between the furnace temperature and 0 °C.

The temperature of the central portion of the furnace, which was held constant to within ±0.01 deg C at the value desired in a particular heat measurement, was measured by a strain-free platinum resistance thermometer (ice-point resistance, about 24 ohms) and a Mueller bridge. The thermometer had been accurately calibrated on the International Temperature Scale of 1948 at the Bureau, and its ice-point resistance was periodically checked throughout the series of calorimetric measurements to guard against the occurrence of unknown significant changes in the calibration.

4. Results

Because of previous knowledge that highly crystalline polytetrafluoroethylene after being heated to the neighborhood of its melting point (about 327 °C) returns to its former thermodynamic state at lower temperatures only with great difficulty if at all, heat measurements on the sample were first made at furnace temperatures not exceeding 300 °C. The heats measured in this first series of measurements, corrected for very small deviations from the standard masses of container parts, are recorded in chronological order in table 1 (column 3). The second series of measurements on the sample was made after the sample had been heated to 340° and then cooled rapidly to 0 °C in the ice calorimeter; the results are recorded in table 2, the heats from individual runs being given for the sample plus container in column 5 and for the empty container in column 6. (The same empty-container measurements are applicable to both series involving the sample, but of course for a given furnace temperature no particular individual measurement with the empty container is to be associated with any particular one with the sample.) Because the relative enthalpy of the polymer sample as measured in this way may depend on the sample history, and actually proved to do so after melting, the lengths of time in the furnace are recorded in both tables 1 and 2, and in addition the chronological sequence of the second series of runs is indicated (table 2, column 2). The successive furnace temperatures of the second series (with the number of runs at each temperature given in parentheses) were thus (in °C) 340° (4), 400° (5), 150° (2), 400° (2), 340° (2), 400° (1), 300° (2), 50° (2), 100° (2), 200° (2), 250° (2), and 440° (4). Since the sample underwent appreciable pyrolysis at 440° (as indicated in column 4 of table 2), no measurements were attempted at higher temperatures. The first runs at 340 and 400 °C showed an upward drift well outside the measurement precision, and are parenthesized because they were not used in computing the mean enthalpy values for the sample given in the last column of the table.

TABLE 1. *Heat measurements on the sample of polytetrafluoroethylene powder before heating to 340 °C*

Furnace temperature t[a]	Time sample in furnace	Individual heat measurement (sample + container)[b]	Mean net enthalpy of sample, $H_t - H_0$ °C
°C	*min*	*J*	*J g⁻¹*
50.00	60	965.9	57.69
	90	966.1	
	20	966.7	
100.00	30	1877.8	108.59
	30	1879.8	
150.00	25	2828.5	162.71
	25	2828.1	
200.00	25	3816.6	220.38
	25	3816.6	
250.00	35	4846.6	281.96
	25	4847.5	
300.00	25	5944.8	350.19
	25	5943.9	

[a] International Temperature Scale of 1948.

[b] The mass of sample was 8.9382g. The corresponding individual heat measurements on the container only are recorded in table 2.

Furukawa, McCoskey, and King [7] recorded their smoothed heat capacities, relative enthalpies, and relative entropies for three of their samples of polytetrafluoroethylene at 5-deg intervals up to 92 °C (except for the transition region 7 to 37 °C). After extrapolating their enthalpies to 100 °C, the enthalpies for the intervals 0–50° and 50–100 °C obtained from the present work (tables 1 and 2, last column) were found to compare with their values as shown in table 3. The present values for the powdered sample agree with theirs within about 0.5 percent. The results after fusion ("quenched") approximate theirs on samples similarly treated, the agreement also being within about 0.5 percent when compared with their value on the annealed sample for 0–50 °C and their value on the molded sample for 50–100 °C.[5]

---

[5] Furukawa, McCoskey, and King [7] recorded no numerical results of their measurements on a sample that had been annealed at 350 °C and then quenched in liquid nitrogen, except over the interval 7–37 °C.

TABLE 2. *Heat measurements on the sample of polytetrafluoroethylene powder after heating to 340 °C*

Furnace temperature t [a]	Sample + container [c]				Container only	Mean net enthalpy of sample, $H_t-H_{0\,°C}$
	Chronological No. of run [b]	Time in furnace	Decrease in sample mass	Individual heat measurement [c]	Individual heat measurement	
°C		min	%	J	J	J g⁻¹
50.00	19	45	0	954.4	451.0	56.37
	20	60	0	954.6	450.2	
100.00	21	55	0	1887.5	908.8	109.67
	22	45	0	1889.4	907.7	
150.00	10	45	0	2862.2	1374.0	166.50
	11	60	0	2862.1	1373.9	
200.00	23	45	0	3877.5	1846.1	227.31
	24	60	0	3879.6	1847.4	
250.00	25	45	0	4943.8	2327.1	292.72
	26	60	0	4942.7	2326.6	
300.00	17	45	0	6096.4	2814.7	366.91
	18	60	0	6091.3	2814.0	
340.00	1	35	0	(7178.0)	3208.0	[f] 452.66
	2	45	0	(7187.0)	3208.8	
	3	90	0	(7193.1)		
	4	[d] 80	0	(7209.0)		
	14	180	0	7253.6		
	15	[e] 195	0	7255.1		
400.00	5	45	0.000	(8569.0)	3811.6	[f] 535.63
	6	60	.003	(8577.9)	3810.1	
	7	90	.004	(8582.0)		
	8	120	.001	8595.1		
	9	150	.002	8599.5		
	12	240	.017	8600.6		
	13	240	.017	8596.7		
	16	45	.000	8600.3		
440.00	27	45	.027	9511.9	4215.7	[f] 593.33
	28	50	.021	(9234.4)	4215.5	
	29	60	.041	9522.0		
	30	90	.043	9522.7		

[a] International Temperature Scale of 1948.

[b] Considering only the runs on the sample + container.

[c] The actual mass of sample was 8.9382 g less the aggregate loss thus far accounted for in column 4. However, for comparison small corrections (by proportion) are included in column 5 to place all the values on the basis of 8.9382 g of sample.

[d] 20 min at 400°, then 60 min at 340 °C.

[e] 45 min at 400°, then 150 min at 340 °C.

[f] Excluding the parenthesized values in column 5.

TABLE 3. *Comparison of enthalpy changes of polytetrafluoroethylene over two 50-degree temperature intervals as determined for various samples by NBS adiabatic and drop calorimetry*

Temperature interval	ΔH for the powdered sample (by adiabatic calorimetry) [b]	Deviation of ΔH from value in column 2						
		Powdered sample			Annealed sample	Quenched sample		Molded sample
		Adiabatic calorimetry (observed) [b]	Drop calorimetry (observed)	Formulated (eq 2)	Adiabatic calorimetry (observed) [b]	Drop calorimetry (observed)	Formulated (eq 5)	Adiabatic calorimetry (observed) [b]
°C	j g⁻¹	%	%	%	%	%	%	%
0–50 [a]	57.9	0.0	−0.4		−2.5	−2.7		−5.2
50–100	50.7	0	+.5	0.0	+4.0	+5.2	+4.7	+4.6

[a] Includes transition region. [b] From reference [7]. The values not so indicated are from the present paper.

An empirical equation of the form

$$H=A+BT+CT^2+D/(E-T), \qquad (1)$$

where T is the temperature in deg K and $A \ldots E$ are constants evaluated by fitting to the data (table 1 or 2, last column), was used to represent the enthalpy H relative to that of some fixed temperature and state, for each of the forms powdered, quenched, and liquid polytetrafluoroethylene. For the liquid the term $D/(E-T)$ was omitted, giving a simple form of equation corresponding to a heat capacity varying linearly with temperature. Since mean observed sample enthalpies are available at only three temperatures in the liquid range (340, 400, and 440 °C), the data were fitted exactly. For each of the two forms powdered and quenched, the mean heat capacity over successive 50-deg intervals obviously increases with temperature at an accelerated rate in the neighborhood of 300 °C (tables 1 and 2), and the term $D/(E-T)$ was arbitrarily introduced to account for this fact. For each of these "solid" forms of the polymer, eq (1) was fit to the observed data at five temperatures (100–300 °C), so that in these cases also the fit was exact.

The enthalpy equations so derived, together with the corresponding equations for heat capacity and relative entropy obtained by differentiation and integration, are as follows. (The units are in terms of joules, grams, and deg K at T °K. Also given are the temperature ranges of applicability, derived as stated below. The subscript "0" applies to 0 °K.)

Polytetrafluoroethylene powder (346.5–573 °K)

$$H_T-H_0=0.54268T+6.715(10^{-4})T^2 \\ +208/(603.4-T)-54.47 \qquad (2)$$

$$C_p=0.54268+1.343(10^{-3})T+208/(603.4-T)^2 \qquad (3)$$

$$S_T-S_0=1.2509 \log_{10} T+1.343(10^{-3})T+0.34/(603.4 \\ -T)-0.0013 \log_{10} (603.4-T)-2.3954 \qquad (4)$$

Quenched polytetrafluoroethylene (332.5–598.33 °K)

$$H_T-H_0=0.54921T+7.2577(10^{-4})T^2 \\ +410.8/(608-T)-61.89 \qquad (5)$$

$$C_p=0.54921+1.45154(10^{-3})T+410.8/(608-T)^2 \qquad (6)$$

$$S_T-S_0=1.2672 \log_{10} T+1.4515(10^{-3})T+0.676/ \\ (608-T)-0.0026 \log_{10} (608-T)-2.4663 \qquad (7)$$

Liquid polytetrafluoroethylene (598.33–713 °K)

$$H_T \text{ (liquid)}-H_0 \text{ (quenched)}=0.61488T \\ +5.97(10^{-4})T^2-12.61 \qquad (8)$$

$$C_p=0.61488+1.194(10^{-3})T \qquad (9)$$

$$S_T \text{ (liquid)}-S_0 \text{ (quenched)}=1.4158 \log_{10} T \\ +1.194(10^{-3})T-2.6576. \qquad (10)$$

The constant terms (integration constants) in the above six enthalpy and entropy equations were evaluated in the following way. First, it may be noted that the enthalpy equations fitted to the data only at higher temperatures cannot be expected to fit the 0–50 °C enthalpy increments, since in this temperature interval large heats of transition are involved. On the other hand each of eqs (2) and (5), while derived without use of the observed 50–100 °C enthalpy increment, actually fits this observed increment within its uncertainty, as seen from table 3. In fact it was found that eq (3) gives at 346.5 °K the same heat capacity for the powder as tabulated by Furukawa, McCoskey, and King [7]. Their enthalpy and entropy at this temperature, relative to 0 °K, were adopted, and the constant terms in eqs (2) and (4) were evaluated so as to satisfy these two respective values.

A similar treatment was performed for the "quenched" sample. Here the choice of a comparable state in the work of Furukawa, McCoskey, and King is not so obvious. Compared with the present "quenched" sample, their "annealed" sample was cooled more slowly whereas it seems not unlikely that their "molded" sample may be more comparable to one which has been cooled more rapidly. Because of this consideration and the fact that their values of each property are very close to each other for the annealed and molded samples at the temperatures in question, these values were averaged. Their average heat capacity is identical with that of eq (6) at 332.5 °K, and so the constant terms in eqs (5) and (7) were evaluated to give agreement with their average values for these respective properties at this temperature. (At 332.5 °K their values of (H_T-H_0), C_p, and (S_T-S_0) are higher for the molded than for the annealed sample by only 0.0 J g^{-1}, 0.007 J g^{-1} deg^{-1} (0.7%), and 0.002 J g^{-1} deg^{-1}, respectively.)

It is reasonable to assume that after run 7 of table 2 (when the enthalpy values ceased to drift) the quenched and liquid forms of sample cooled to the same thermodynamic state, and hence the same enthalpy, in the ice calorimeter. The further assumption was made that either the powdered or quenched sample, when heated, undergoes no *isothermal* melting but passes gradually into the liquid state. The equations for the enthalpy of the two forms relative to 0 °C give identical values at 598.33 °K. This temperature was assumed to be the actual melting point (temperature of complete conversion to liquid), and the constant terms in eqs (8) and (10) were so determined that these equations would give the same values at this temperature as eqs (5) and (7), respectively.

It may be noted that in eqs (4), (7), and (10) the entropy is expressed relative to that at 0 °K. Unlike many simple crystalline substances, polytetrafluoroethylene undoubtedly possesses some residual entropy owing to random molecular orientations. Its magnitude is unknown, but it may be small.

Values of heat capacity, relative enthalpy, and relative entropy given by eqs (2)–(10) at even temperatures are listed in tables 4 and 5. Curves of heat capacity calculated from eqs (3), (6), and (9) are compared with the results of earlier investigators in figure 1.

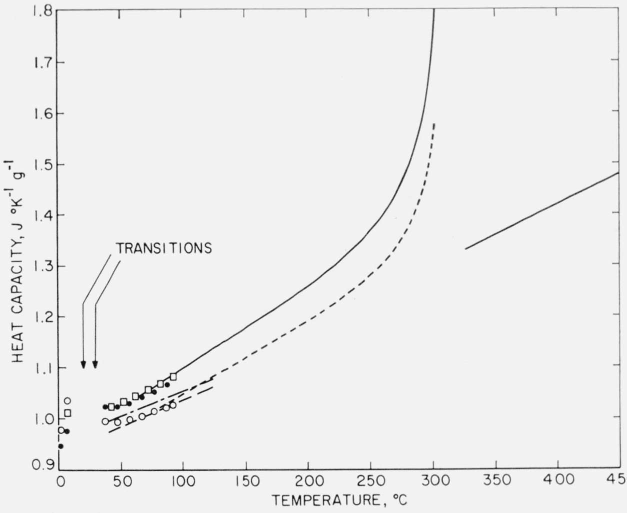

FIGURE 1. *Heat capacity of polytetrafluoroethylene.*

- - - -, powder (this work); ———, quenched and liquid (this work); 0, powder (Furukawa, McCoskey, and King [7]); ●, annealed (Furukawa, McCoskey, and King [7]); □, molded (Furukawa, McCoskey, and King [7]); — — —, powder (Marx and Dole [8]); — - — -, drawn (Marx and Dole [8]).

TABLE 4. *Heat capacity, enthalpy, and entropy of polytetrafluoroethylene powder (calculated from eqs 2–4)*

T	C_p	H_T-H_0 [a]	S_T-S_0 [b]
$°K$	$J\,°K^{-1}\,g^{-1}$	$J\,g^{-1}$	$J\,°K^{-1}\,g^{-1}$
350	1.016	218.6	1.255
360	1.030	228.8	1.284
370	1.043	239.1	1.312
380	1.057	249.6	1.340
390	1.071	260.3	1.368
400	1.085	271.1	1.395
425	1.120	298.6	1.462
450	1.156	327.1	1.527
475	1.193	356.4	1.591
500	1.234	386.8	1.653
525	1.282	418.2	1.714
550	1.354	451.0	1.775
575	1.573	486.9	1.839

[a] Assuming a value of 215.0 $J\,g^{-1}$ at 346.5 $°K$ [7].
[b] Assuming a value of 1.245 $J\,°K^{-1}\,g^{-1}$ at 346.5 $°K$ [7].

TABLE 5. *Heat capacity, enthalpy, and entropy of quenched and liquid polytetrafluoroethylene (calculated from eqs 5–10)*

T	C_p	H_T-H_0 [a]	S_T-S_0 [b]
$°K$	$J\,°K^{-1}\,g^{-1}$	$J\,g^{-1}$	$J\,°K^{-1}\,g^{-1}$
340	1.048	210.3	1.231
350	1.063	220.8	1.262
360	1.078	231.6	1.292
370	1.094	242.4	1.322
380	1.109	253.4	1.351
390	1.124	264.6	1.380
400	1.139	275.9	1.409
425	1.178	304.8	1.479
450	1.219	334.8	1.548
475	1.262	365.8	1.615
500	1.310	398.0	1.681
525	1.371	431.4	1.746
550	1.470	466.8	1.812
575	1.761	506.3	1.882
600 [c]	1.331	571.2	1.992
625	1.361	604.9	2.047
650	1.391	639.3	2.101
675	1.421	674.4	2.154
700	1.451	710.3	2.206
725	1.480	747.0	2.258

[a] Assuming a value of 202.45 $J\,g^{-1}$ at 332.5 °K [7].
[b] Assuming a value of 1.208 $J\,°\mathrm{K}^{-1}\,g^{-1}$ at 332.5 °K [7].
[c] The polytetrafluoroethylene was assumed to be liquid above 598.3 °K.

5. Discussion

The annealing of polytetrafluoroethylene has usually been carried out at temperatures of 350 °C or higher. From table 2 (column 5) it can be seen that the enthalpy values in individual measurements at 340 °C continued to increase steadily with time, by increments each many times the precision ordinarily obtained, during the first four runs at this temperature, and did not become constant until after four runs at 400 °C, when all subsequent values at either temperature were constant within the precision of measurement.

These drifts with time of the apparent relative enthalpy of the liquid might off-hand be attributed mainly to one of three causes: (1) The shorter times in the furnace may have been insufficient to establish thermal equilibrium; (2) the sample may in different measurements have "solidified" to different enthalpy states in the ice calorimeter; or (3) the state of the liquid may have been changing significantly. As to the first possibility, it was estimated from "relaxation-time" tests made at 100° and 150 °C that the sample + container should have had time to acquire its full enthalpy within one joule in 20 min in the furnace at either 340 or 400 °C, accounting for the absorption of the heat of fusion. In each actual measurement the time was always much greater. As to the second possibility, the rates of cooling the sample in the calorimeter were no doubt similar in different measurements, and at any rate probably varied randomly. The authors have carried out drop calorimetry on several materials having known phase diagrams which clearly predict this type of behavior, but invariably the enthalpy values obtained varied randomly with time. These arguments leave only the third possibility, which suggests that, unlike atomic and small-molecule substances, the polymer even after melting does not reach any structural equilibrium rapidly, but at a given temperature slowly absorbs still more energy in a virtual continuation of the fusion process. This is probably not surprising in view of the large number of relative positions the long polymer chains can assume even in a high state of disorder.

In contrast to the large enthalpy drifts observed at 340 and 400 °C, the two enthalpy values obtained on the powdered sample at 300 °C (table 1) show excellent agreement (to 0.03 percent). Although no measurements at lower temperatures were subsequently repeated before the sample began annealing at 340°, there is no evidence that the powdered sample underwent appreciable irreversible annealing at 300°. As pointed out in section 2, the enthalpy values at this temperature are higher by several joules per gram than would be predicted from an extrapolation of the values at and below 200 °C. This effect was treated as a reversible partial fusion.

Returning to table 2, the first enthalpy value obtained at 440 °C is appreciably lower than the last two. (The second value is assumed to involve an accidental error.) Even though the enthalpy had apparently stabilized at 340 and 400°, it is possible that some small further change in the liquid state occurred at 440 °C, a possibility that introduces some uncertainty into the slope of the heat capacity-temperature curve of the liquid. However, from 340 to 440 °C there is no correlation between weight losses and enthalpy changes which suggests such a real change.

Lupton has given an equation of state for liquid polytetrafluoroethylene (cited in reference [1]):

$$(P+a)(V-b)=B(T-c), \tag{11}$$

where a=400 atm, b=0.500 cm^3 g^{-1}, c=144 °C,[6] and B=0.306 cm^3 atm g^{-1} deg^{-1}. At 600 °K table 5 gives for the liquid C_p=5.30 cal deg^{-1} (g atom)$^{-1}$. Using this value, the thermodynamic relation

$$C_p-C_v=T(\partial P/\partial T)_v(\partial V/\partial T)_p, \tag{12}$$

---

[6] c was 156 °C for a sample of very high molecular weight.

and Lupton's equation gives $C_v=4.90$ cal deg^{-1} (g atom)$^{-1}$, which is 82 percent of the equipartitional value $3R$ corresponding to the limiting high-temperature three-dimensional harmonic oscillation of all the atoms in polytetrafluoroethylene. A single harmonic oscillator which gives a heat capacity at 600 °K that is 82 percent of the equipartitional value has a frequency of 650 cm^{-1}. Actually, the frequency spectrum of polytetrafluoroethylene is known to cover a wide range below and above this frequency [1], and in addition the above value of C_v may include small contributions from structural changes with temperature.

The weight losses observed at 400 and 440 °C in the present work (table 2, column 4) are at rates five to ten times smaller than those found by Madorsky and his coworkers [16, 17]. Siegel, Muus, Lin, and Larsen [18] also have recently reported rates of pyrolysis of polytetrafluoroethylene, and at 380 °C find the rate much smaller in the presence of C_2F_4 gas at a pressure of 35 mm Hg than in vacuum, as well as a weight *gain* when the partial pressure of C_2F_4 was 80 mm. These results suggest some reversibility of the decomposition reaction. Siegel et al. also used available thermodynamic data to calculate pressures of C_2F_4 in equilibrium with the polymer from 327 to 712 °C. Their equilibrium pressure at 380 °C ($\leq$0.1 mm) indicates that there should have been a gain instead of a loss of weight in the experiment at 35 mm, and suggests that either their calculated equilibrium pressures are in error by large factors or else that the volatilization reaction observed to occur at this pressure was predominantly other than that of liquid polytetrafluoroethylene to C_2F_4 gas. While the present authors have no way of knowing what the pressure of C_2F_4 was in contact with their own sample, they estimate that also in this case the pressure of the gas was probably sometimes many times the corresponding listed equilibrium pressure. The substitution of the heat capacities found in the present work for those estimated by Siegel et al. would have very little effect on the calculated equilibrium pressures. One assumption involved in their calculations is that the residual entropy ($S_{0\,°\mathrm{K}}$) of the polytetrafluoroethylene powder measured by Furukawa, McCoskey, and King [7] was zero. If this was not true, the correction would *lower* the calculated equilibrium pressures of C_2F_4.

The one important piece of enthalpy data missing from the present investigation is the heat of fusion of crystalline polytetrafluoroethylene. In drop calorimetry the heat measured is that involved in *cooling* the sample; and it is evident that the powdered sample, once melted, never returned to its original state in the calorimeter. So far as is known, no one has measured the crystalline heat of fusion of this polymer calorimetrically, at least with any real accuracy. This could be done in precise heating types of calorimetry, though these are not often used at such elevated temperatures. The heat of fusion could be obtained also from the heats of combustion in fluorine of a sample that had been fused and one that had not been (together with the use of the appropriate heat-capacity data), but the heat of such a combustion is approximately 200 times the heat of fusion and hence the combustion calorimetry would need to be not only highly precise but also on entirely comparable samples.

As mentioned in section 1, the heat of fusion of polytetrafluoroethylene has been calculated using PVT data and the Clapeyron equation. The published values vary from 35 to 85 J g^{-1}, but the value of Lupton [10], 57.3 J g^{-1}, seems to be considered the best value [18].

In section 4 the simple type of temperature function $D/(E-T)$ (last term of eq (1)) was introduced to represent the accelerated increase of enthalpy with temperature (presumably as a result of partial fusion) of the two solid forms of the polymer. This function is of the form which to a good approximation represents the "premelting" of a great many low-molecular-weight substances contaminated with one or more foreign phases ("impurities") which are insoluble in the solid phase but soluble in the liquid phase of the principal component. Leaving open for the moment the question of how much justification there is in extending this interpretation to the broad melting observed for such a high polymer as polytetrafluoroethylene, it is appropriate to attempt to test empirically the validity of the $D/(E-T)$ enthalpy term, since it should account for the total heat of fusion when T reaches the observed melting point of the polymer, where fusion is complete.

According to the thermodynamic theory of dilute solutions, the heat of fusion L_f is given approximately by

$$L_f=DT_m/E\,(E-T_m), \tag{13}$$

TABLE 6. *Values of the melting points and heats of fusion of the polytetrafluoroethylene samples calculated from the formulated results (eqs 1, 2, 4, 5, 8, 10, 13) using alternative assumptions*

Sample	Basic assumption	Calculated temperatures		Calc. heat of fusion of sample, L_f
		E	Calc. sample melting point, T_m	
		°C	*°C*	*J g^{-1}*
Powdered	Using Lupton's heat of fusion [10]	330.2	326.6	(57.3)
	Enthalpy of powdered and quenched identical at 0 °K		326.7	58
	Entropy of powdered and quenched identical at 0 °K		327.1	65
Quenched	Enthalpy at 0 °C independent of furnace temperature	334.8	325.2	41

where D and E have values as in eq (1), T_m is the actual equilibrium melting (or freezing) point of the material, and E is the corresponding temperature for the completely "pure" substance. Using the thermal results of this paper as formulated by eqs (2)—(10), eq (13) and each of several alternative assumptions described below were used to calculate values for the sample melting point and the heat of fusion, which are recorded in table 6.

The first such calculation was made assuming Lupton's value of the crystalline heat of fusion stated above. Equations (2) and (13) then give $T_m=$ 326.6 °C. An alternative calculation can be made after assuming a definite relation between the enthalpies or entropies of different forms of the polytetrafluoroethylene sample. According to the accurate low-temperature calorimetric data of Furukawa et al. [7], the values of $(H_{310^\circ K}-H_{0^\circ K})$ and $(S_{310^\circ K}-S_{0^\circ K})$ are respectively only 0.4 and 0.2 percent different for the powdered form compared with the annealed and molded forms. If the powdered and quenched forms are assumed to have the same enthalpy at 0 °K, one can equate eqs (2) and (8) and get $T_m=326.7$ °C, which when substituted into eq (13) gives $L_f=58$ J g^{-1} (1 percent higher than Lupton's value). Or, if the entropies at 0 °K are assumed equal, one gets from eqs (4), (10), and (13) $T_m=327.1$ °C and $L_f=65$ J g^{-1} (the latter being 13 percent higher than Lupton's value). As for the *quenched* polymer, it was assumed (section 4) that its enthalpy when in the ice calorimeter was essentially identical to that of the liquid similarly cooled; this suggests equating eqs (5) and (8), which gives $T_m=325.2$ °C and (from eq (13)) $L_f=41$ J g^{-1}, or only some 70 percent of the values for the heat of fusion of the powdered form. Independent results on the polymer indicate that the quenched sample must have been much less crystalline than the powdered one, but the larger heat capacities of the former at lower temperatures may reflect further substantial contributions from the fusion process over a very wide temperature range.

It is striking that the three values in table 6 for the melting point of the powdered polymer are all 327 °C, for this is the generally accepted value based on direct observation but it was nowhere assumed in the above calculations. A simple "premelting"-type enthalpy term, then, appears to provide a satisfactory fit to the available thermodynamic data for crystalline polytetrafluoroethylene. The agreement noted lends weight to the approximate validity of eqs (2) and (5) as empirical extrapolations of the thermal data above 300 °C. Such equations may represent well the total *enthalpy* interval from 300 to 340 °C, the temperatures of the actual measurements, and the uncertainty as to how this enthalpy change is distributed over the 40-deg interval introduces but little uncertainty into the corresponding *entropy* increment (probably less than 0.002 J g^{-1} deg^{-1} in the present case). However, the *heat capacity* undoubtedly increases sharply within the interval and so is highly uncertain at many of these temperatures.

Below the melting point of a macroscopic crystal its free energy is less than that of the corresponding quantity of the pure supercooled liquid. Hence, if some fusion of the sample occurs at such a temperature, additional effects must be present which remove this free-energy inequality. In the ordinary type of premelting discussed above, a "foreign" phase can dissolve in the liquid formed and thereby lower the free energy of the latter. Incidentally, the theory of dilute solutions on which the ordinary treatment of premelting is based does not require that "chemical" impurities be present. A nominally pure substance may behave thermodynamically as a multicomponent system, and undergo broad melting, if two or more molecular forms are present which convert into one another only sluggishly.

On the other hand, in recent years experimental and theoretical evidence has been obtained that substantial amounts of certain high polymers show melting-point depressions because the free energy of certain portions of the solid is "abnormally" enhanced by effects not present in the resulting liquid. The principal such effects are believed to be crystal defects, other high-energy structural features such as chain folds, and especially the presence of platelike crystals so thin that their surface free energies are appreciable compared with their bulk free energies. A recent paper by Hoffman [19] discusses in detail these and other theoretical aspects of polyethylene and polychlorotrifluoroethylene. Such thin platelike crystals are known to be present in polytetrafluoroethylene too. It thus appears that the accelerated upturn in the heat-capacity curves of the solid forms of polytetrafluoroethylene, reported in the present paper and attributed to partial fusion, could be explained as being the result of the melting of thin crystals having a suitable distribution of thicknesses. (It should be noted, however, that each of these heat measurements was repeated with high reproducibility, so that it would be necessary to assume that the thin crystals were reformed in the same or an equivalent distribution upon subsequent cooling and recrystallization.)

It may well be that both ordinary "impurity" premelting (where the impurities affect the free energy of the liquid phase) and surface-free-energy effects (which affect the free energy of the crystalline phase) combine to cause the broad melting effect observed in polytetrafluoroethylene.

The authors are particularly indebted to C. A. Sperati, of E. I. du Pont de Nemours and Company, who carried out several tests on the sample of polytetrafluoroethylene used, and to John D. Hoffman, of the National Bureau of Standards, who reviewed the manuscript and made several helpful criticisms.

6. References

[1] C. A. Sperati and H. W. Starkweather, Jr., Fortschr. Hochpolym.-Forsch. **2,** 465 (1961) (in English).

[2] P. E. Thomas, J. F. Lontz, C. A. Sperati, and J. L. McPherson, J. Soc. Plastics Eng. **12,** 89 (1956).

[3] C. J. Speerschneider and C. H. Li, J. Appl. Phys. **33,** 1871 (1962).

[4] R. K. Eby and K. M. Sinnott, J. Appl. Phys. **32,** 1765 (1961).

[5] W. E. Hanford and R. M. Joyce, J. Am. Chem. Soc. **68,** 2082 (1946).

[6] N. K. J. Symons, J. Polymer Science **51,** S21 (1961).

[7] G. T. Furukawa, R. E. McCoskey, and G. J. King, J. Research NBS **49,** 273 (1952) RP2364.

[8] P. Marx and M. Dole, J. Am. Chem. Soc. **77,** 4771 (1955).

[9] P. L. McGeer and H. C. Duus, J. Chem. Phys. **20,** 1813 (1952).

[10] J. M. Lupton, 134th meeting of the Amer. Chem. Soc., Chicago, Ill., Sept. 1958. (See references [1], [11], and [18].)

[11] H. W. Starkweather, Jr., and R. H. Boyd, J. Phys. Chem. **64,** 410 (1960).

[12] W. Brandt, J. Chem. Phys. **26,** 262 (1957).

[13] Yu. Ya. Gotlib and I. V. Sochava, Dokl. Akad. Nauk SSSR **147,** 580 (1962).

[14] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Research NBS **57,** 67 (1956) RP2694.

[15] D. C. Ginnings and R. J. Corruccini, J. Research NBS **38,** 593 (1947) RP1797.

[16] S. L. Madorsky, V. E. Hart, S. Strauss, and V. A. Sedlak, J. Res. NBS **51,** 327 (1953) RP2461.

[17] S. L. Madorsky and S. Strauss, J. Res. NBS **64A,** 513 (1960).

[18] J. C. Siegel, L. T. Muus, T. P. Lin, and H. A. Larsen, J. Polymer Science **2A,** 391 (1964).

[19] J. D. Hoffman, Trans. Soc. Plastic Eng. **4,** 315 (1964).

(Paper 69A2–336)